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Comment on "Stabilizing platinum atoms on CeO_2 oxygen vacancies by metal-support interaction induced interface distortion: mechanism and application" by Jiang et al., *Appl. Catal., B* 2020, *278*, 119304

A recent paper in this journal reported on the catalytic activity of presumably single Pt atoms dispersed on three different ceria supports, each of those exposing a different crystal termination [1]. The Pt_1-CeO_2\{100\} sample displayed an activity for methanol oxidation higher than that of the two other materials. The authors attributed the higher activity of this sample to a greater distortion of the ceria-Pt_1 interface, favoring atomic dispersion of Pt.

Unfortunately, two important flaws can be found in the analysis of the data regarding the characterization of the samples by IR of CO adsorption. First, a band at 2116 cm^{-1} was assigned to CO adsorbed on Pt_1-CeO_2 (Fig. 1 Bottom, which relates to both Fig. 1d and 6 in reference [1]). This band is actually due to the P-branch of the rotovibrational spectrum of gas-phase CO (Fig. 1, Top), which always exhibits two branches (P and R) [2], the positions of which slightly depend on temperature [3]. Note that the authors had correctly assigned the band at 2169 cm^{-1} to gas-phase CO, which is the corresponding R-branch. Large gas-phase contributions are often observed when using DRIFTS and those can be easily removed according to a procedure described elsewhere [3] to reveal solely the DRIFTS spectra of adsorbed species. Thus, the current DRIFTS analysis reported by Jiang et al. cannot be used to support the presence of isolated atoms (whether or not those are present) on any of the three samples, since the gas-phase signal of CO overwhelms that of adsorbates.

The second flaw is more serious as a band at ca. 2058 cm^{-1} (Fig. 1, red arrow), not mentioned by the authors, can be seen only in the case of the most active catalyst Pt_1-CeO_2\{100\}. A band at this position strongly suggests the presence of Pt clusters or nanoparticles on the sample [4]. The use of high calcination temperatures led to more obvious bands between 2000 and 2100 cm^{-1}, related to new Pt° and PtOx clusters and nanoparticles [5], through the agglomeration of the Pt isolated atoms, as proposed by the authors.

Note that a band at 2058 cm^{-1} present after reduction carried out in DRIFTS cell could also indicate the formation of volatile $Ni(CO)_4$ [6], by reaction of CO with metallic nickel contained in the steel of the cell [7].

Recent reports on Pt/CeO_2 indicated that the TOF for CO oxidation at low temperatures of Pt nanoparticles on ceria can be several orders of magnitude higher than that of Pt_1/CeO_2, [4, 8]. This indicates that a minor concentration of Pt nanoparticles can be totally responsible for the catalytic activity, among a majority of essentially inert Pt_1 species. In consequence, the likely presence of Pt nanoparticles on the most active catalyst used here for methanol oxidation raises doubt that this activity could be attributed solely to Pt_1. A comparison between the TOF measured for nanoparticles and single atoms should be provided to determine which of those is the most active species.

Therefore, the conclusions that the higher activity measured over the Pt_1/CeO_2\{100\} is specifically due to the CeO_2\{100\} nanostructure around isolated Pt atoms is not supported by the data reported in the paper, as the presence of Pt (or even Ni) nanoparticles on this most active sample cannot be excluded.

Declaration of Competing Interest

The author declares no conflict of interest.

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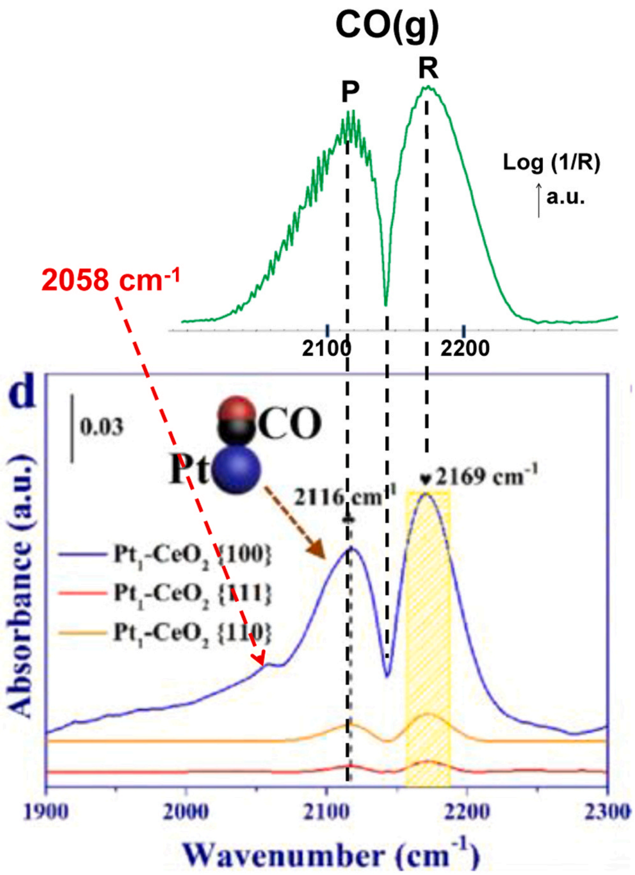

Fig. 1. Comparison of (Top, green spectrum) the gas-phase spectrum of CO at 50 °C and (Bottom) the spectra reported in Fig. 1d. by Jiang et al. in reference [1].

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